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REACTION RATE DATA

Number 59

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Number 59

February 1977

This issue of the DASIAC Reaction Rate Data presents summaries of recent progress for investigations supported by the Defense Nuclear Agency in portions of its Reaction Rate Program, plus summaries of related work submitted by other non-DNA-funded investigators. Formal DNA reports (where indicated) may be purchased from the Defense Documentation Center, Cameron Station—Building 5, Alexandria, Virginia 22314; alternatively, the information contained in such reports may be obtained subsequently from pertinent articles published in the open scientific and technical journals.

The major portion of this document usually is composed of a number of informal, bimonthly technical progress reports comprising information and data which are considered to be preliminary in nature and may be subject to possible future revision and/or changes. It is requested that recipients do not cite or reference the contents of this issue in other media without receipt of prior specific approval by the author and organization involved. This professional courtesy has been, and will continue to be, greatly appreciated by all contributors, especially those who intend to publish formally elsewhere at a later date.

Submission of subsequent technical progress reports, and/or other pertinent information relevant to those DNA-supported efforts reported herein deemed appropriate for publication consideration in future editions of the DASIAC Reaction Rate Data is welcome, and should be sent directly to DASIAC, Attn: A. Feryok, General Electric Company—TEMPO, 816 State Street, Santa Barbara, California 93102, which is a DoD-approved activity that is contractually engaged by the Defense Nuclear Agency for this purpose.

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PART I – DNA-SPONSORED RESEARCH

Progress through November 1976

A. Subtask S99QAX HD 010

"Reaction Rates Critical to Propagation"

1. *Measurements of Rate Coefficients for Two Body Positive Ion-Negative Neutralization – J. Peterson, SRI (Work Unit 69 in FY 76; Work Unit 79 in FY 77).*

During the period July 6 to August 13, 1976, Dr. Merle N. Hirsh was on the staff of SRI as a Visiting Scientist, with the purpose of assessing the reliability of ion-ion neutralization measurements. He examined the three conflicting experiments dealing with the mutual neutralization of atmospheric positive and negative ions: the SRI merging beams experiment, the Dewey stationary afterglow, and the Birmingham flowing afterglow experiment. The latter two experiments were found to suffer from the effects of negative-ion chemistry which proceeds in competition with the recombination reactions. A computer simulation of the stationary afterglow which includes chemical reactions was attempted, but it was not possible to model the experimental data sufficiently well. The lack of understanding of the negative ion chemistry which plagues computer ionospheric simulations is active here to prevent accurate modeling of the recombining/reacting ions. An effective ionic recombination rate coefficient was deduced from the afterglow decay of NO^+ , for its collective recombination with NO_2 , $\text{NO}_2 \cdot \text{H}_2\text{O}$, NO_3 , and $\text{NO}_3 \cdot \text{H}_2\text{O}$; this effective rate is $(1.8 \pm 0.5) \times 10^{-7} \text{ cm}^3/\text{sec}$, considerably larger than the $(0.5 \pm 0.1) \times 10^{-7} \text{ cm}^3/\text{sec}$ measured in the flowing afterglow. The unknown chemistry greatly complicates the analysis of the negative ion decays, but preliminary results suggest the following approximate coefficients for recombination of NO^+ with the individual negative ions: NO_2 : (1-2); NO_3 : (5-8); $\text{NO}_2 \cdot \text{H}_2\text{O}$: (0.1-0.5); $\text{NO}_3 \cdot \text{H}_2\text{O}$: (0.1-1), all $\times 10^{-7} \text{ cm}^3/\text{sec}$.

Dr. Hirsh concluded that although the merging beams experiment may suffer from vibrational excitation, it is still the only unequivocal way to separate chemical reactions from the desired mutual neutralization.

At the end of October we were visited by a consultant, Dr. David Smith of Birmingham, England, who has been able to measure ion-ion neutralization rates for some ions of ionospheric interest in a flowing afterglow apparatus. For the cases of $\text{NO}^+ + \text{NO}_2$ and $\text{NO}^+ + \text{NO}_3$, the only pairs that we have also studied, his rate constants differ from those deduced from our merged-beams results. We spent two days familiarizing each other with the details of the two experimental approaches and related problems. We also discussed ideas for future attacks on the ion-ion neutralization problem with cluster ions.

Experimentally, we have been reconstructing the merged-beams apparatus, returning to a configuration which was previously used for the simpler ions, and preparing it for use in taking a second look at $\text{NO}^+ + \text{NO}_2$ and $\text{NO}^+ + \text{NO}_3$, to determine the cause of the disagreement with the Birmingham results. We are now evaluating the performance of the apparatus with O^+ and O^- beams, whose cross sections we have measured previously. Tests are being conducted on beam shapes and overlap, and on the detection electronics. Neutral reaction products have been detected, but the true ion-ion neutralization signal has not yet been successfully separated from the beam-beam intermodulation effects. Several seemingly minor but actually pernicious electrical and vacuum problems,

as well as mechanical problems, inside the vacuum chambers have caused delays. On the brighter side, we have ordered a new, vector lock-in amplifier with SRI funds for use on this project, which will aid in the synchronous detection of the very weak ion-ion neutralization signal.

2. *Recombination of Electrons - Cluster Ions, and Ion-Molecule Reactions* - M. Biondi, University of Pittsburgh (Work Unit 71 in FY 76; Work Unit 81 in FY 77).

Electron-Ion Recombination Studies

The rebrazing of the copper microwave-afterglow apparatus to repair small leaks was not successful, since the copper walls have become porous from numerous high-temperature, ultrahigh vacuum processing cycles. As a result it has been necessary to design, construct, and test a new, stainless steel microwave afterglow cavity which employs numerous Conflat flanged ports to give flexibility in installing design changes for different experiments. The new cavity has successfully passed its preliminary tests and is being employed in the $\text{H}_3\text{O}^+(\text{H}_2\text{O})_n$ electron temperature dependence recombination studies.

Ion-Molecule Reaction Rates

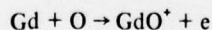
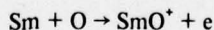
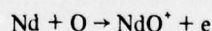
The high temperature drift tube has been giving us problems at 1000K. In addition to the heavy thermionic emission which leads to alkali ion generation and attendant space charge effects, the tantalum walls of the tube warped enough after prolonged use at high temperature to cause excessive gas leakage at the tantalum-sapphire pressure seals. It has been necessary to disassemble the entire apparatus and remachine the warped surfaces to the desired flatness to ensure proper gas seals. In addition, modifications were made to improve gas density measurements within the high-temperature drift tube portion of the apparatus.

The studies of the $\text{O}^+ + \text{N}_2 \rightarrow \text{NO}^+ + \text{N}$ reaction at high temperatures have now been resumed.

3. *Associative Ionization Reactions of Communications Importance* - W. Fite, Extranuclear Labs (Work Unit 72 in FY 76; Work Unit 82 in FY 77).

Efforts during the past reporting period have been directed toward resolving some of the larger discrepancies in the atomic oxygen associative ionization cross sections measured by H.H. Lo at the University of Pittsburgh and by R.B. Cohen *et al* at Illinois Institute of Technology. We received a letter from Dr. Cohen providing absolute cross sections for many of the reactions studied by his group. These values are relative to cross section for the reaction $\text{Gd} + \text{O} \rightarrow \text{GdO}^+ + \text{e}$, measured by Lo and Fite [*Chem. Phys. Lett.* 29, 39 (1974)].

We examined the three reactions



by making direct comparisons of the cross sections for each of the three possible pairs of metals. The following ratios were obtained:

$$Q(\text{Nd})/Q(\text{Gd}) = 3.2$$

$$Q(\text{Gd})/Q(\text{Sm}) = 4.9$$

$$Q(\text{Sm})/Q(\text{Nd}) = .11$$

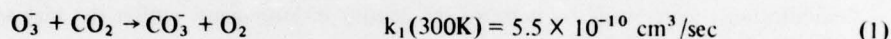
While these ratios are not corrected for differences in the metal atom electron impact cross sections, the product of the three ratios should be unity. The experimental product, 1.7, is indicative of a reasonably high degree of experimental consistency. Using these ratios and the previously measured Gd-O cross section yields cross sections of $2 \times 10^{-15} (Q_{\text{Nd}}^e/Q_{\text{U}}^e) \text{ cm}^2$ for Nd and $2 \times 10^{-16} (Q_{\text{Sm}}^e/Q_{\text{U}}^e) \text{ cm}^2$ for Sm, where the Q^e 's are the electron impact ionization cross sections for the metals. While the experimental ratios may appear to indicate greater accuracies, we feel that a factor of two is a more reasonable estimate due primarily to the effects of the unknown source temperatures on the experimental cross section.

These results are in much better agreement with those of Cohen *et al* than the earlier measurements by Lo, which points out the need to run two metals simultaneously. Our Sm value is a factor of 5 larger than Cohen's but this difference may be attributable to the five-element chain of ratios used by Cohen in comparing Sm and Gd.

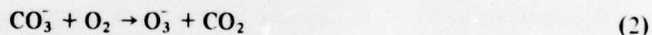
A preliminary attempt to collect and energy analyze electrons liberated in an associative ionization reaction has been made using parallel plates with a retarding grid. Technical difficulties have thus far precluded the observation of reaction electrons; however, we understand the nature of the problems and simple solutions are available.

4. *Investigation of Negative Ion Reaction Rates; Effects of Vibrational Excitation Energy - E. Ferguson et al, NOAA (Work Unit 73 in FY 76; Work Unit 88 in FY 77).*

The reaction



is quite important in atmospheric negative ion chemistry. Recent measurements indicate that the energies to dissociate O from O_3^- and CO_3^- are similar [i.e., $D(\text{O}^- - \text{CO}_2) = 1.8 \pm 0.1 \text{ eV}$ and $D(\text{O}^- - \text{O}_2) = 1.7 \pm 0.1 \text{ eV}$]. This in turn, implies that reaction (1) is almost thermoneutral. As a consequence, the reaction in the reverse direction



could be significant even at low temperatures in the atmosphere, where the concentration of O_2 exceeds the CO_2 concentration by a factor of 10^3 . We have attempted to measure k_2 with the following results:

1. In the variable temperature flowing afterglow we find $k_2 < 5 \times 10^{-16} \text{ cm}^3/\text{sec}$ for $T < 600\text{K}$.
2. In the flow-drift system $k_2 < 8 \times 10^{-12} \text{ cm}^3/\text{sec}$ for $\text{K.E.}_{\text{cm}} = 0.5 \text{ eV}$. These results indicate that reaction (2) is of no importance in low-temperature ionized air-like gas mixtures.

A systematic study of the effects of ion speed distributions in drift tube studies of ion-neutral reaction has been in progress in the flow-drift system. The first phase of this investigation, the study of the reactions of O^+ with N_2 , O_2 , and NO in rare gas buffers, has been completed. For O^+ ions drifting at nonthermal E/N values in helium and argon, the measured rate constants agree well with theoretical predictions of the effects of nonMaxwellian ion speed distributions, implying that these kinetic effects are properly interpreted and understood and that nonMaxwellian ion speed distributions of atomic ions now pose no problem in the interpretation and application of ion-neutral rate constants measured in drift tubes using atomic buffer gases.

As part of the D-region negative ion chemistry reinvestigation, the following O_3 reactions have been measured at 300K:

Reactions	Rate (10^{-10} cm ³ /sec)		
	Present	Previous	
$O^- + O_3 \rightarrow O_2^- + O_2$ $\rightarrow O_3^- + O$	8.8	5.3	(3)
$OH^- + O_3 \rightarrow O_3^- + OH$	9.5		(4)
$O_2^- + O_3 \rightarrow O_3^- + O_2$	6.0	4.0	(5)
$NO_2^- + O_3 \rightarrow NO_3^- + O_2$	0.9	0.18	(6)

The estimated uncertainty in the present determinations is 40 percent. Reactions (3), (4), and (6) have been previously measured in the flowing afterglow and the present results are somewhat larger. For reactions (3) and (5) the differences are within experimental uncertainty and the agreement is considered adequate. In reaction (3), O_2^- production was observed to be a major (~50 percent) reaction channel. For reaction (6), the present results are a factor of five larger than the previous determination. This larger discrepancy is most likely due to an error in the determination of the rate of O_3 addition in the earlier measurements. Reaction (5), which has not been previously studied in our laboratory, is of considerable interest, since it establishes a firm lower limit for the electron affinity of O_3 , i.e., $EA(O_3) \geq EA(OH) = 1.83$ eV. This limit agrees with several recent determinations of $EA(O_3)$, which place the electron affinity of O_3 about 2.1 eV.

In addition to the O_3 reactions, the following NO_2 reactions have been measured:

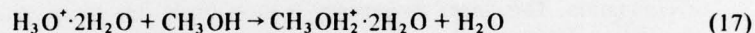
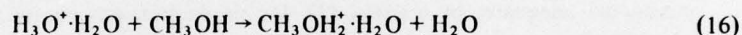
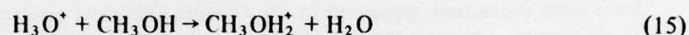
Reactions	Rate (10^{-10} cm ³ /sec)		
	Present	Previous	
$O^- + NO_2 \rightarrow NO_2^- + O$ $\rightarrow O_2^- + NO$	9.6	12	(7)
$O_2^- + NO_2 \rightarrow NO_2^- + O_2$	6.5	8	(8)
$OH^- + NO_2 \rightarrow NO_2^- + OH$	11	10	(9)

The present results have an estimated uncertainty of 40 percent. These reactions have all been investigated previously in the flowing afterglow and the agreement is good.

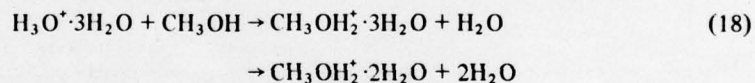
At present, there is very little information available concerning the negative ion-chemistry of chlorine and its compounds. Although these compounds, Cl , HCl , and ClO , are expected only in trace amounts in the ionosphere ($\sim 10^7$ HCl molecules/cm³ at 60 km), they can nevertheless be important reactant neutrals, because the negative ions produced are quite stable. The following reactions involving HCl have been measured in the room temperature flowing afterglow:

Reaction	Rate (10^{-10} cm ³ /sec)	
$O^- + HCl \rightarrow Cl^- + OH$	18 ± 9	(10)
$O_2^- + HCl \rightarrow Cl^- + HO_2$	17 ± 7	(11)
$NO_2^- + HCl \rightarrow Cl^- + HNO_2$	12 ± 4	(12)
$CO_3^- + HCl \rightarrow \text{products}$	<0.3	(13)
$CO_4^- + HCl \rightarrow Cl^- + HO_2 + CO_2$	11 ± 4	(14)

Current atmospheric models predict that significant concentrations of H_2CO are present in the stratosphere as by-products of the oxidation of methane and the possibility of large concentrations of CH_3OH has been suggested. Since the proton affinities of these compounds are larger than those of H_2O their presence has important implications for stratospheric ion chemistry. The reactions

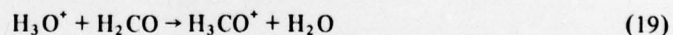


have been studied as a function of ion kinetic energy in the flow-drift system. The reactions are fast at all energies. At 300K, $k_{15} = 1.7 \times 10^{-9}$ cm³/sec, $k_{16} = 1.8 \times 10^{-9}$ cm³/sec, and $k_{17} = 1.7 \times 10^{-9}$ cm³/sec. The estimated uncertainty in these measurements is 50 percent. The reaction



has been investigated in the flowing afterglow as is found at 300K to be fast, $k_{18} \sim 1 \times 10^{-9}$ cm³/sec.

In addition, the reaction



has been studied in the flowing afterglow. This measurement gives $k_{19} = 2.2 \times 10^{-9}$ cm³/sec with an estimated uncertainty of a factor of two.

5. *Applications of the AIRCHEM Computer Code – J. Heimerl et al, BRL (Work Unit 74 in FY 76; Work Unit 84 in FY 77).*

To avoid the relatively long execution times and the large computer memory/core requirements necessary in the execution of a detailed, multispecies model, it is desirable to have a simpler model which can produce similar numerical results. We have been interested in the charged particle chemistry in the stratosphere and mesosphere (20-90 km) under quiet or undisturbed conditions. Mitra and Rowe's semiempirical model of the mid-latitude D-region (65-80 km), developed for a wide range of excitation conditions, could not simply be extended to encompass our altitudes of interest. Thus we have constructed a code consisting of the six ions: NO^+ , O_2^+ , O_4^+ , X^+ , e , O_2^- , and X^- . Our approach has been to use the multispecies model results as a guide in this construction. We have attempted to

incorporate rate coefficients of fundamental reactions as the linking parameters between the ions and so avoid the "lumped parameter" approach with its concomitant loss of physical understanding. This approach also permits the identity of X^+ and X^- to change as a function of altitude as the multispecies code predicts. For example, X^- can be identified as O^- at 90 km and as CO_3^- at 50 km. Presently our six-ion code satisfactorily reproduces the profiles of the major charged species of the multispecies code.

We have employed the Benchmark version of the AIRCHEM code to observe the effects of decade changes (i.e., $\times 10^{\pm 1}$) in selected ion-ion recombination coefficients upon the more populous, computed positive and negative ion concentrations. Comparisons were made against computations which used a nominal value of $2 \times 10^{-7} (T/300)^{0.5} \text{ cm}^3/\text{sec}$ for unmeasured coefficients. The ionization case selected used $10^{11} \text{ electrons/cm}^3$ for "prompt" excitation while the delayed excitation was given by

$$Q(t) = Q_0 (1 + t)^{-1.2} ,$$

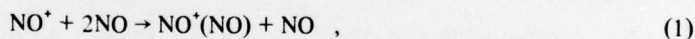
ion-pairs/cm³/sec, $Q_0 = 10^8$. The altitude range and time domain considered were 30 to 80 km and 10^0 to 10^4 seconds, respectively.

At each altitude decade the more populous ions (those $\geq \sim 10$ percent of the total) were identified and paired. The ion-ion recombination coefficients corresponding to these pairs were then simultaneously altered by factors of ten.

Raising or lowering the selected rate coefficients generally produced little variation in a particular ionic species' percentage contribution to the total ion density. However, variations approaching a factor of two were found at isolated times and altitudes. A BRL report detailing these findings is in preparation.

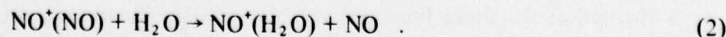
6. *Positive and Negative Ion Reactions, Photodissociation Reactions Hindering Cluster Ions* — J.A. Vanderhoff et al, BRL (Work Unit 75 in FY 76; Work Unit 85 in FY 77).

Further measurements of the photodissociation cross section of $NO^+(NO)$ have been made. It has been found that the cross section can vary with laser power and E/N. This dependence is thought to arise from the reaction for the formation of $NO^+(NO)$,



coupling into the photodissociation process. Since the cross section for the reaction $NO^+(NO) + h\nu \rightarrow NO^+ + NO$ is extremely large over the region from 750 to 500 nm the rate of production of $NO^+(NO)$ can be accelerated when a large fraction of the $NO^+(NO)$ is broken up into NO^+ and NO (high power). In a similar fashion E/N controls the time an ion is subject to the photon flux and thus for low values of E/N reaction (1) has a longer time to repopulate $NO^+(NO)$ at a larger effective rate. To obtain reliable photodissociation cross sections experimental conditions were arranged to minimize these effects.

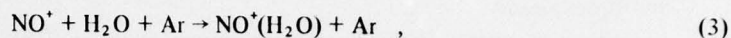
Studies of the photodissociation cross section for $NO^+(H_2O)$ revealed a drift distance dependent cross section at photon wavelengths of both 647.1 nm and 530.9 nm. The cross section decreases with increasing drift distance. The gas mixture in which these measurements were made was 350 mTorr NO with a trace of H_2O . For this gas mixture the formation of $NO^+(H_2O)$ proceeded via reaction (1) followed by



It is known that $NO^+(NO)$ has a large photodissociation cross section at these wavelengths, thus the $NO^+(NO)$ is substantially depleted over the laser beam volume when the laser is on. This reduces

the production of $\text{NO}^+(\text{H}_2\text{O})$ by reaction (2) and thus can cause an apparent photodissociation cross section independent of possible photodissociation of $\text{NO}^+(\text{H}_2\text{O})$.

When $\text{NO}^+(\text{NO})$ was formed using small amounts of NO and H_2O in an Ar buffer the dominant reaction to form $\text{NO}^+(\text{H}_2\text{O})$ was



i.e., $\text{NO}^+(\text{NO})$ was not an important intermediate species. In this case photodissociation was not observed for $\text{NO}^+(\text{H}_2\text{O})$ at 647.1 nm.

Preliminary measurements for the photodestruction of O_3^- have been made for various photon energies. These cross sections are listed in Table I. It is apparent that the cross section for O_3^- exhibits abundant structure.

Table I

Photon Energy (eV)	Cross Section (10^{-18} cm^2)
2.18	1.1
2.34	4.4
2.38	4.7
2.41	4.2
2.57	8.5
2.60	6.3
2.62	6.7
2.65	9.7
2.66	11.0
2.71	7.5
2.73	9.9
3.0	3.2
3.5	1.6

Experimental data for the clustering of Na^+ to CO_2 over the E/N range of 10 to 150 Td have been obtained. The analysis of these data is under way.

7. *Ion-Neutral Investigations* – E. Murad, J. Paulson, AFGL (Work Unit 78 in FY 76; Work Unit 83 in FY 77).

Work was continued on photodissociation of N_2O^+ using a frequency-doubled tunable dye laser. Several peaks have now been observed in the wavelength region from 295 to 341 nm. The time-of-flight (TOF) spectra of the NO^+ product ions have been measured, and analysis of the optical and TOF spectra is in progress to determine the vibrational levels of the dissociating ions. The first of two papers on this work has been completed. Attempts to observe photodissociation of NO_2^+ at 445 nm and 375 nm have been unsuccessful. Upper limits to the cross sections at these wavelengths are $5 \times 10^{-20} \text{ cm}^2$ and $15 \times 10^{-19} \text{ cm}^2$, respectively.

Work was continued on the collisional dissociation of CO_3^- and on the reaction of CO_3^- with O_2 giving O_3^- and CO_2 . Cross sections were measured for both of these channels in collisions with O_2 and for the collisional dissociation reactions with N_2 and the rare gases. The observed dissociation cross sections near threshold were compared with expected cross sections obtained by convoluting a theoretical threshold function with the velocity distribution of the neutral reactant. The results give a dissociation energy for CO_3^- of 2.1 eV, i.e., about 0.3 eV higher than that obtained from the SRI photodissociation experiments. The cross section for production of O_3^- in collisions of CO_3^- with O_2 was found to be less than $0.03 \times 10^{-16} \text{ cm}^2$ at relative energies up to about 1 eV, but increased to about $0.5 \times 10^{-16} \text{ cm}^2$ at 6 eV.

B. Subtask S99QAX HD 028

"Theoretical Investigations of Ionizing Mechanisms in the Upper Atmosphere"

1. *Theoretical Aspects of SRI Laboratory Ion-Ion Measurements – F. Smith et al, SRI (Work Unit 38 in FY 76; Work Unit 41 in FY 77).*

The theoretical study is directed to improving the tidal distortion model for the neutralization rate of hydrated and other cluster ions. Using a semiclassical theory based on perturbation methods, we are delineating the domains in which simpler approximations give good agreement with other methods including the computer-limited quantal close coupling calculations. The semiclassical perturbation method agrees with the Born approximation in its region of validity, provides corrections to it of comparatively simple form, and is successful over a much wider domain. We are now examining other limiting forms, including one that is applicable in the moderate energy region (from thermal to many eV) when the interaction strength or the heavy mass of the particles causes the Born approximation to break down. For ions (or electrons) impinging on polar targets, this new limiting case has a very simple form. While the Born expression for the rotational excitation cross section from $j - \frac{1}{2}$ to $j + \frac{1}{2}$ is proportional to $(4/3)\beta^2 \ln(4/g)$, where $\beta = m\mu e/h^2$ depends on the dipole moment μ , and $g = h^2/2IE(2j+1) = \Delta E_{\text{rot}}/E$ depends on the energy E and moment of inertia I , the expression in the new limit is $\sim (4/3)\beta^2 [\ln(4/\beta g) - 1]$. We expect it to be a valuable prototype for the exploration of interactions in more complicated cluster ions.

2. *Investigations Relevant to the "Twilight Anomaly" and Other Relevant Problems – W. Swider, AFGL (Work Unit 39 in FY 76; Work Unit 42 in FY 77).*

The current fast NO^+ ion chemistry espoused by certain groups was applied to the nighttime PCA'69 results. The reduction in NO^+ ions was too great as compared to the data, about an order of magnitude difference. Hence, we see no reason to retract any conclusions drawn in the analysis of the data, published in the February 1976 issue of the *Journal of Geophysical Research*. As stated previously, even with the use of the fast NO^+ ion chemistry, cold temperatures and a high water vapor mixing ratio, 10^{-5} , we have been unable to obtain effective electron loss rates as great as those reported for the August 1972 SPE.

Ion composition data for upleg, and deduced nitric oxide concentrations, were published for ICECAP 73A, rocket A18.205-1. There has been some interest recently in the downleg data. Narcisi's downleg data shows that the ionic ratio NO^+/O_2^+ is 2.5 (180 km), 4.0 (150 km), 5.0 (130 km), 8.0 (117 km) and 60 (110 km). The quality of data deteriorates below this height because of rocket turnover and shock problems. Ion concentrations measured by the plasma frequency probe at these altitudes were $6 \times 10^4 \text{ cm}^{-3}$ (180 km), 1×10^5 (150 km), 1.2×10^5 (130 km), 1.4×10^5 (117 km) and 9×10^4 (110 km). Using the theoretical steady-state relationship between the ratios NO/e and NO^+/O_2^+ , estimated NO concentrations for downleg are $2.2 \times 10^7 \text{ cm}^{-3}$ (150 km), 6×10^7 (130 km), 2.4×10^8 (117 km) and 2.2×10^9 (110 km) with CIRA 1972 as the neutral gas background. These concentrations are within a factor of two of the NO estimates on upleg which, in general, contained much higher electron concentrations. However, there is no doubt that the upleg electron concentrations are more accurate, wake problems and other effects complicating the downleg results. Hence our downleg estimates of NO must be viewed with caution.

C. Subtask S99QAX HI 002

"Atomic and Molecular Physics of IR Emissions"

1. Fine Definition of IR Spectra for Certain Metal Oxide Species – D.W. Green et al, Argonne National Laboratory (Work Unit 28 in FY 76; Work Unit 39 in FY 77).

Previous work has shown that UO_2^+ is produced by the reactions $\text{UO} + \text{NO}_2$, $\text{UO}_2 + \text{NO}_2$ and $\text{UO}_2 + \text{NO}$ in Ar matrices. The production of UO^+ is thermodynamically favorable via the following reaction, $\text{U} + \text{NO}_2 \rightarrow \text{UO}^+\text{NO}^-$. Experimental work has been directed toward the production of UO^+ by cocondensing U atoms produced by a sputtering device with NO_2 in Ar matrices at 14K.

In these studies, spectral lines have been observed including several that could be assigned to reaction products of species in the matrix. Among the lines were some that did not have ^{18}O counterparts when N^{18}O_2 was used in place of N^{16}O_2 (spectrum A of Figure 1). The species responsible for these lines have now been identified as UN, UN_2 and a species labeled "X-UN" which contains one N-atom, no O-atoms and probably one U-atom. As shown in spectra B and C in Figure 1, these species were also produced when a uranium metal hollow cathode was sputtered with N_2/Ar mixtures. A manuscript entitled "The Identification of UN in Ar Matrices," which has been accepted for publication in *J. Chem. Phys.*, describes these results.

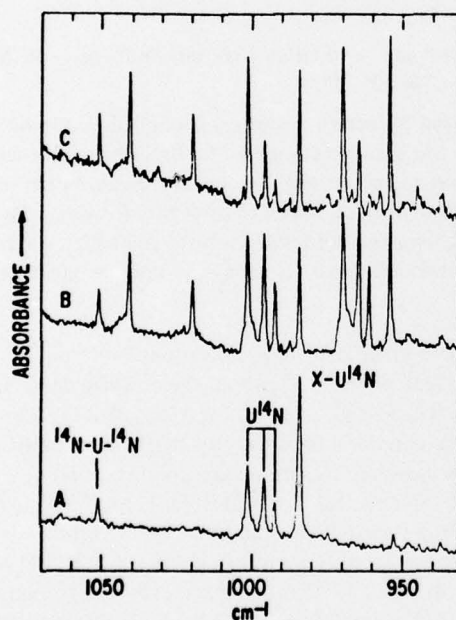


Figure 1. Infrared spectra obtained from an Ar matrix at 14K. (A) the products of cocondensation of U atoms with NO_2 ; (B) the products of sputtering U with a 1:1:800 $^{14}\text{N}_2$: $^{15}\text{N}_2$:Ar mixture; (C) the same matrix as (B) after annealing to 30K and recooling to 14K.

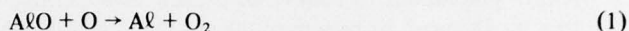
In an effort to gain further insight into the nature of the reactions of $\text{U} + \text{NO}_2$, the reactions of U atoms with ^{14}NO and ^{15}NO have also been studied. Although a number of absorption peaks could not be assigned, it now appears that products other than UO^+ are favored in the $\text{U} + \text{NO}_2$ and $\text{U} + \text{NO}$ reactions.

An alternative method to produce UO^+ is presently being studied. The photolysis of HI in solid Ar yields free iodine atoms. The subsequent charge transfer reaction with UO to produce the UO^+I^- ion pair appears to be thermodynamically favorable. Experimental studies to produce UO^+ by this method are ready to begin.

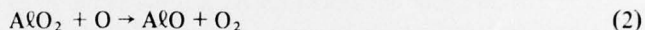
2. *Reactions Between AlO and O Atoms – A. Fontijn et al, AeroChem (Work Unit 29 in FY 76; Work Unit 40 in FY 77).*

In previous work we obtained the rate coefficients of the Al/O_2 and AlO/O_2 reactions in the 300-1700K range in high-temperature fast-flow reactors (HTFFR). Since the fate of gaseous AlO_x ($x = 0, 1, 2$) and its effects in disturbed atmospheres can also depend on its reactions with O atoms, we are obtaining kinetic information on these reactions.

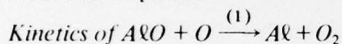
To calculate an upper limit for the rate coefficient of the O-atom abstraction reaction



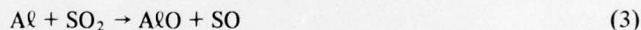
a study of the Al/SO_2 reaction has been made to determine a lower limit for $D(\text{Al}-\text{O})$ and hence a lower limit to the activation energy, E_A , of reaction (1). Data at 700K indicate $D(\text{Al}-\text{O}) \geq 128$ kcal mole⁻¹ and hence E_A for reaction (1) is ≥ 10 kcal mole⁻¹, making it essentially an infinitely slow process at temperatures of interest. This high value for $D(\text{Al}-\text{O})$ suggests that O-atom abstraction from AlO_2



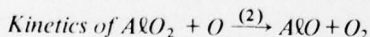
is also negligibly slow and therefore of little interest in modeling disturbed atmospheres. We have not yet succeeded in elucidating the mechanism of the Al-oxidation chemiluminescence (or the identity of the emitter), but the rates of the reactions observed in this investigation suggest that O-atom addition to Al and/or AlO may well be important in determining Al oxide concentrations in disturbed atmospheres.



Measurements for the rate coefficient of the reaction



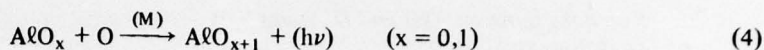
at 700K have been completed. The range of pressures used for this measurement was 3 to 75 Torr. The value $k_3(700\text{K}) = (7.2 \pm 60\%) \times 10^{-12}$ ml molecule⁻¹ sec⁻¹ has been obtained. As discussed in the preceding status report a value of this magnitude for k_3 requires $D(\text{Al}-\text{O}) \geq 128$ kcal mole⁻¹. This in turn implies that reaction (1) is at least 10 kcal mole⁻¹ endothermic and hence k_1 is negligibly small at temperatures of interest. The above assumes a gas kinetic (3×10^{-10} ml molecule⁻¹ sec⁻¹) pre-exponential for k_3 ; most likely the actual pre-exponential is lower and hence $D(\text{Al}-\text{O})$ larger. This question can be settled by extending the k_3 measurements to lower temperatures and obtaining a direct measurement of the activation energy.



The only determination of $D(\text{O}-\text{AlO})$ is based on the equilibrium $\text{Al} + \text{AlO}_2 \rightleftharpoons 2\text{AlO}$ which, on the basis of the previously accepted value for $D(\text{Al}-\text{O})$ of 121.5 ± 1 , leads to $D(\text{O}-\text{AlO}) = 121.5$ kcal mole⁻¹. Since we now find $D(\text{Al}-\text{O}) \geq 128$ kcal mole⁻¹ it appears that $D(\text{O}-\text{AlO})$ also ≥ 128 kcal mole⁻¹. This suggests that reaction (2) is also too slow to influence $[\text{AlO}_x]$ in disturbed atmospheres.

Chemiluminescent and Overall O-Addition Reactions

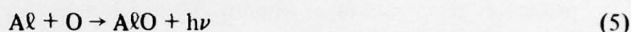
Since the influence of the abstraction reactions (1) and (2) on atmospheric $[\text{AlO}_x]$ is apparently negligible, addition reactions of the type



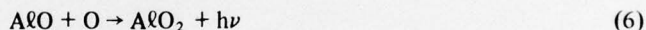
appear of increased potential importance for disturbed atmospheres. We are presently approaching the study of reactions (4) by observations of the chemiluminescence.

The present measurements are made at $\approx 325\text{K}$, $[\text{Al}] \approx 10^{10} \text{ ml}^{-1}$ and $[\text{O}] \approx 10^{14} \text{ ml}^{-1}$ in Ar/N_2 baths at ≈ 3 Torr. As discussed in our last report, the intense chemiluminescence observed in the Al/O system decreases monotonically in intensity upon addition of O_2 ; we have now taken extensive precautions to remove all possible external sources of O_2 (impurities, leaks) and confirmed that no O_2 need be present in the system to produce the chemiluminescence. However, in view of subsequent results (below) this observation now appears less relevant to the reaction mechanism.

The rate coefficient for light emission, based on initial $[\text{Al}]$, is 10^{-13} to $10^{-14} \text{ ml molecule}^{-1} \text{ sec}^{-1}$ for the "formal" addition reaction



The effective rate coefficient for Al removal in the Al/O system under the above operating conditions has been found to be at least as high as that for light emission. On this basis the radiative recombination reaction (5) could be considered as the source of the continuum chemiluminescence. A rate coefficient on the order of $10^{-13} \text{ ml molecule}^{-1}$ at first appears unreasonably high for a radiative recombination reaction. However, very long-lived complexes have been observed previously in two-body association reactions involving metal atoms, i.e., between Group IIA (alkaline earth) metals and halogen (diatomic) molecules. These triatomic complexes can be stabilized by emission of (continuum) radiation. Complex lifetimes $\geq 10^{-4} \text{ sec}$ occur and cross sections on the order of $\approx 10^{-19} \text{ cm}^2$, corresponding at 325K to rate coefficients of $\approx 10^{-14} \text{ ml molecule}^{-1} \text{ sec}^{-1}$, have been observed.* It may be that such an excited complex is formed in reaction (5). However, the alternate two-body radiative recombination reaction



appears more probable than reaction (5) since it involves a triatomic complex. We previously concluded that AlO is not involved in the chemiluminescent reaction since O_2 addition to the Al/O system only leads to decreases in intensity, while the Al/O_2 reaction is an efficient source of AlO . However, the present observation of a rapid reaction between Al and O probably invalidates that conclusion.

A few experiments were made to investigate the possible involvement of dimers in the chemiluminescence. A heated coil ($T \geq 1000\text{K}$) was placed in the source section downstream from the Al source coil from which such species could have evaporated. Since the Al-Al bond energy is only 2 eV such a coil should lead to dimer dissociation. The small decreases (up to a factor of 2) observed in light intensity were apparently not due to the slight heating of the reaction zone which occurred simultaneously. A more quantitative check of the involvement of Al_2 in the chemiluminescence is needed.

Elucidation of the reaction mechanism also requires that the $[\text{O}]$ in the reaction zone after Al addition be known. Due to the strong intensity of the Al/O emission it was not possible to measure $[\text{O}]$ via the O/NO light intensity. $[\text{O}]$ measurements could probably best be made using resonance fluorescence or absorption.

*Such long-lived complexes should also give rise to increased three-body rate coefficients due to the proportionally longer period available for collisional stabilization.

To complete the investigation of the Al-oxidation chemiluminescence it appears necessary to make simultaneous measurements of chemiluminescence intensity and: (i) $[Al]_{rel}$ and $[O]_{rel}$; (ii) $[AlO]_{rel}$ and $[O]_{rel}$; (iii) $[Al_2]_{rel}$ and $[O]_{rel}$; and to make similar observations on the apparently related Al/N continuum chemiluminescence. AlO and Al_2 can both be measured via laser-induced fluorescence and Al and O, via atomic fluorescence or absorption. While these techniques have already been used in our DNA work (though not yet for Al_2 and O) this combination of measurements is far beyond the scope of the present contract in which we initially concentrated on reaction (1) and the determination of $D(Al-O)$.

3. *UV and VUV Photoabsorption and Photoionization Investigations* - R. Huffman, AFGL (Work Unit 30 in FY 76; Work Unit 35 in FY 77).

During this period, the relationship of rocket- and ground-based optical and ultraviolet measurements to ionospheric irregularities such as striations has been discussed in association with the work of the PhotoMetrics contract. The available rocket photometers and other instrumentation have been assessed. New, compact detectors offering spatial resolution, being developed for this laboratory, have been utilized in calculations of diagnostic capabilities for F-region electron density and other ionospheric characteristics.

The content of the photodissociation chapter for the DNA Reaction Rate Handbook has been discussed.

4. *Analysis of UV and X-Ray Data for O_2 and O_3* - L. Weeks, AFGL (Work Unit 31 in FY 76; Work Unit 36 in FY 77).

The ozone paper, "Ozone Measurements in the Stratosphere, Mesosphere, and Lower Thermosphere during ALADDIN 74," by L.H. Weeks *et al.*, is being prepared for submission to *JGR*. The paper summarizes the ozone environment during ALADDIN 74 and points out some large differences between data and representative models of ozone during quiet conditions. It is found, however, that the 81-km inversion is reasonably well represented by various models compared to data at higher and lower altitudes, which is more poorly modeled.

Data analysis from the ICECAP 76 rockets is in progress. Preliminary processing for rocket A10.507-1 is complete, and work is now underway on A10.504-1. The first analysis will be of the mesospheric ozone profile and its relation to the earlier PCA 69 results.

5. *Recombination Rate, Energy Transfer to N_2 and O_2 from Vibrationally Excited NO^+* - M. Camac, F. Bien, Aerodyne (Work Unit 32 in FY 76, Work Unit 37 in FY 77).

Work has restarted to measure the vibrational transfer of $NO^+(v)$ to N_2 . A new diode laser has been obtained which tunes over vibration-rotation lines of the $v = 0$ to $v = 4$ levels of NO^+ . The NO^+ , formed through photoionization of NO, is monitored through absorption. Thus, by knowing the locations of the various vibration-rotation lines of interest, the relative concentrations of the $NO^+(v)$ is measured as a function of time. The relative absorption coefficient, as well as quenching by N_2 , and dissociative recombination rates of the several vibrations levels are thus determined.

The work during this period has centered on the calibration of the new diode laser. The exact location of each vibration-rotation line will be determined through calibrating with the known CO_2 absorption spectra.

Due to the multiline emission spectra of the laser, a monochromator has been placed in the optical path. This monochromator also allows the further calibration of the NO^+ line locations. A system of ultraviolet light monitoring has been devised which measures the total photon flux from each ultraviolet flash lamp used in the photoionization of NO. The UV lamps (Lyman lamps) have been redesigned to have aerodynamic windows between the gas discharge and the MgF_2 windows. The MgF_2 windows which were damaged by metallic sputtering have been repolished and their

transmissions checked using a transmissometer. A new simultaneous UV detector of the ionization gage design has been substituted for the previous UV detectors.

The new UV detector allows the simultaneous monitoring of each of the six Lyman lamps during each experimental run. This detector actually monitors the NO^+ ion concentration within the long path absorption cell during the experimental run, giving a direct measure of the NO^+ concentration produced by photoionization. This detector is similar to the UV detector used during previous lamp calibrations; however, six units are now used simultaneously during each experimental run, one in front of each lamp, to allow simultaneous measurement of all six lamps rather than taking an integrated average of light from those lamps.

In spite of previous setbacks, the measurement of the radiative lifetime of $\text{NO}^+ v = 2, 3, 4$, and 5 is being carried out on schedule and should be completed by the next reporting period. The transfer of vibrational energy to N_2 will be carried out in the following period.

6. *Reactions of Excited Atmospheric Gases* -F. Kaufman, University of Pittsburgh (Work Unit 33 in FY 76; Work Unit 38 in FY 77).

Our paper on the kinetics of hydronium ion clustering reactions was published in *J. Chem. Phys.* 65, 2715 (1976). It presents new information on the rate constants of the reaction sequence $\text{H}_3\text{O}^+(\text{H}_2\text{O})_{n-1} + \text{H}_2\text{O} + \text{He} \rightarrow \text{H}_3\text{O}^+(\text{H}_2\text{O})_n + \text{He}$ for $n = 1$ to 4 at 298K, showing that k increases from $6.65 \times 10^{-28} \text{ cm}^6 \text{ sec}^{-1}$ for $n = 1$ to 1.51×10^{-27} for $n = 2$, but remains constant at 1.5×10^{-27} for $n = 3$. It was also possible to measure the difference between the diffusion coefficients of H_3O^+ and of $\text{H}_3\text{O}^+(\text{H}_2\text{O})_3$ and to interpolate the values for the other hydrates to yield $D_{a,n} = 798, 638, 584$, and $554 \text{ cm}^2 \text{ torr sec}^{-1}$ for the ambipolar diffusion coefficients at 1 torr in the sequence $n = 1$ to 4. A paper on two- and three-body reactions of various ions (He^+ , Ar^+ , O^+ , N^+ , N_2^+ , N_2H^+ , N_4^+ , H_3^+ , and NO^+) with D_2O is in preparation.

The tunable dye laser fluorescence and lifetime studies of NO_2 have provided several important results. (1) The variably nonexponential behavior of the emitted fluorescence following excitation in the red (578 to 612 nm) comes from a single electronically excited state, $^2\text{B}_2$, which appears to be highly perturbed by and mixed with vibrationally excited ground state, $^2\text{A}_1$. As expected, the nonexponentiality (experimentally fitted to a biexponential decay) is most pronounced when strong features of the known $^2\text{A}_1 \leftarrow ^2\text{B}_2$ bands are being excited. This can be explained by the Bixon and Jortner mechanism of variable vibronic coupling between $^2\text{B}_2$ and $^2\text{A}_1$, and removes, in part, the long-debated anomaly between the measured radiative lifetime and the integrated absorption coefficient for absorption in the red. (2) Collisional relaxation processes are now also being studied by observing the fluorescence through a small grating monochromator in such a way that there is a minimum of optical discrimination against those molecules which emit after fairly long delay times. With excitation at 532 nm and observation with 0.5- to 3-nm band width, we see clearly how the well characterized, banded features become relatively less prominent compared to a pseudo-continuous background emission which peaks broadly about 4 to $5 \times 10^3 \text{ cm}^{-1}$ to the red of the exciting line at pressures of about 1 mtorr. This is in disagreement with some recent claims that the discrete and continuous features of the fluorescent emission are collisionally relaxed with roughly equal efficiency. (3) Lifetime and spectral information is also being gathered, for the first time, in the presence of other collision partners such as helium. The latter appears to be very efficient at quenching the discrete features which suggests that a rotational relaxation process is involved.

The characterization of a number of vacuum UV resonance lamps in terms of a modified Doppler-Doppler model as a function of excitation frequency (rf versus microwave), power, and gas pressure (helium) has provided important results. These lamps, such as those used in the Apollo-Soyuz ultraviolet absorption experiment, are shown to have increasingly broad line shapes as their pressure is decreased below 1 torr. For example, an rf excited oxygen lamp 0.2 torr of He (with a trace of oxygen) has an apparent emission "temperature" of about 4300K so that large errors

would be incurred if that T_E were assumed to be near 500K. Near 20 torr pressure, T_E is reduced to about 650K. A combination of processes, including electron impact of O, dissociative excitation of O_2 by He metastables and cascading from higher excited states, is being used to explain these data whose importance arises from the increasing use of such resonance lamps in field and laboratory experiment.

PART II – ABSTRACTS OF RELEVANT REPORTS

1. *Temperature Dependence of AlO_2 and AlO/O_2 Kinetics* – A. Fontijn, W. Felder, and J.J. Houghton, AeroChem Research Labs, Inc.

Report No. RADC-TR-76-212

July 1976

Rate coefficients for the reactions $Al + O_2 \rightarrow AlO + O$ and $AlO + O_2 \rightarrow AlO_2 + O$ show agreement with previous determinations in a high-temperature fast-flow reactor at 1000 to 1700 and at 1400K, respectively. This report presents the results of investigations at temperatures as low as 310K. The reaction rate for $Al + O_2 \rightarrow AlO + O$ was determined to be $(3 \pm 2) \times 10^{-11}$ ml per molecule per second. The reaction rate for $AlO + O_2 \rightarrow AlO_2 + O$ was determined to be $(5 \pm 3) \times 10^{-11}$ ml per molecule per second over the 310 to 1400K temperature range.

2. *The Clustering of O_2 and He to Li^+* – L.M. Colonna-Romano and G.E. Keller, Ballistic Research Laboratories.

Report No. BRL 1882

May 1976

The clustering of oxygen and helium to positive lithium ions has been studied using a drift tube-mass spectrometer at 319K. For oxygen clustering, the rate coefficients for cluster ion formation and collisional dissociation were measured as a function of E/N. For clustering to helium, only an equilibrium constant was determined. The relative importance of the clustering of several atmospheric gases to positive lithium ions in the ionosphere is discussed.

3. *The Ion Pair Production Rate due to Cosmic Rays* – M.G. Heaps (BRL/NRC Research Associate), Ballistic Research Laboratories.

Report No. BRL MR 2641

June 1976

Galactic cosmic rays are the primary source of ionization in the stratosphere at all times and are the primary source in the lower mesosphere at night and during solar eclipses. The ion-pair production rate is given as a simple function of latitude and height (using pressure as the variable). The solar cycle variation may be included by use of a simple sinusoidal variation.

4. *AIRCHEM: A Computational Technique for Modeling the Chemistry of the Atmosphere* – E.L. Lortie, M.D. Kregel, and F.E. Niles, Ballistic Research Laboratories.

Report No. BRL 1913

August 1976

Deionization processes thought to describe the real-time concentrations of ion and neutral constituents in the ionized stratosphere and mesosphere can be modeled numerically by a number of techniques of varying complexity and efficiency. One very efficient technique for complex cases is the AIRCHEM computer program. The AIRCHEM program utilizes the K-method for solving the ordinary differential equations which arise from the mathematical description of atmospheric

deionization processes, many of which are characterized by exceedingly short time constants. This report serves to give the mathematical description of atmospheric deionization as modeled by AIRCHEM and also serves as a user's manual for those interested in using the program. Included is a complete FORTRAN listing of the AIRCHEM program along with sample input and the corresponding output from a sample run.

5. *Chemistry of Atmospheric Deionization Outside Intermediate-Altitude Fireballs; II. 15-, 20-, and 25-km Altitude* – F.E. Niles, Ballistic Research Laboratories.

Report No. BRL 1909

August 1976

Number densities for 59 atmospheric species during the deionization of the atmosphere outside the fireball from a high-yield nuclear burst at an altitude of 30 km have been calculated using the AIRCHEM computer code and are reported for altitudes of 15, 20, and 25 km and horizontal ranges of 0, 1, 5, 10, 20, and 30 km. Equivalent lumped parameters are calculated for each decade in time from 1 microsecond to 1000 seconds and compared with the lumped parameters employed in the WEPH D computer code. Important reactions at three major intervals of time during atmospheric deionization are identified.

6. *Computed Results for Disturbed Atmospheric Conditions at 60 km* – F.E. Niles, J.M. Heimerl, Ballistic Research Laboratories.

Report No. BRL IMR 510

July 1976

Electron, positive ion, negative ion and neutral densities have been computed as a function of time and ionization conditions at an altitude of 60 km. The delayed electron production Q is given by $Q_0(1 + t)^{-1.2}$, where t is in seconds. Q_0 was assigned the values 10^6 , 10^8 or 10^{10} ion-pairs $\text{cm}^{-3} \text{sec}^{-1}$. The prompt electron density, N_0 , was assigned the values 10^{11} , 10^{10} or 10^8 cm^{-3} subject to the condition $|N_0| > |Q_0|$. Selected results and limited comparisons are reported together with the variations of the computed equivalent rate coefficients with time and ionization conditions.

7. *Photodissociation of $\text{O}_2^+(\text{H}_2\text{O})$* – J.A. Vanderhoff and R.A. Beyer (NRC/BRL) Resident Research Associate, Ballistic Research Laboratories.

Report No. BRL MR 2642

June 1976

The photodissociation cross section of the weakly bound positive ion cluster $\text{O}_2^+(\text{H}_2\text{O})$ has been measured at 15 discrete energies between 1.833 and 2.727 eV. Measurements indicate the cross section increases smoothly from 0.6 to $6 \times 10^{-18} \text{ cm}^2$ over this energy range. These cross section values are the largest reported for a positive ion cluster of atmospheric importance.

8. *Ion-Molecule Association Reactions Involving NO^+ and H_2S , SO_2 , OCS , SF_6 , N_2O , CO , or Xe* – J.A. Vanderhoff, M.S. Miller, and J.M. Heimerl, Ballistic Research Laboratories.

Report No. 1886

May 1976

Quantitative measurements have been made of the three-body association rate coefficients for the clustering of hydrogen sulfide, sulfur dioxide, carbonyl sulfide, sulfur hexafluoride, nitrous oxide, carbon monoxide, and xenon to the positive nitric oxide ion at 296K. Selective photoionization of nitric oxide in nitric oxide-hydrogen sulfide, and nitric oxide-sulfur dioxide gas mixtures resulted in the formation of a family of cluster ions. Ion mass spectra are given and interpreted for these two gas mixtures. Rearrangement reactions occur in the nitric oxide-hydrogen sulfide gas mixture to produce protonated hydrogen sulfide positive ions and protonated ammonia positive ions. No rearrangement reactions were observed in the nitric oxide-sulfur dioxide mixture.

9. *Parameterization of the Atmospheric Heating Rate from 15 to 120 km due to O₂ and O₃ Absorption of Solar Radiation* – D.F. Strobel, Naval Research Laboratory.

Report No. NRL MR 3398

November 1976

The atmospheric heating rate due to O₂ and O₃ absorption of solar radiation is parameterized with an accuracy of ± 5 percent in the altitude region 15 to 120 km. For relevant wavelengths the effects of multiple scattering and ground reflection are also included. These parameterizations are computationally fast, efficient, and suitable for use in numerical models of atmospheric circulation.

10. *Recombination of Electrons with NH₄⁺(NH₃)_n-Series Ions* – C.-M. Huang, M.A. Biondi, R. Johnsen, University of Pittsburgh.

Report No. ARO 11166.7-P

September 1976

The recombination coefficients α of NH₄⁺(NH₃)_n-series ions for $n = 0$ to 4 have been determined using a microwave afterglow-mass-spectrometer apparatus. For NH₄⁺ ions, under conditions where the electron, ion, and neutral temperatures are equal ($T_e = T_+ = T_n$), $\alpha(18^\circ) = (2.5 \pm 1)$, (1.5 ± 0.3) and $(1.3 \pm 0.2) \times 10^{-6}$ cm³/sec at 200, 300, and 410K, respectively. The electron-temperature dependences of the recombination coefficients for the first and second cluster ions are found to be (in cm³/sec) $\alpha(35^\circ) = 2.82 \times 10^{-6} [300/T_e(K)]^{-0.147}$ and $\alpha(52^\circ) = 2.68 \times 10^{-6} [300/T_e(K)]^{-0.050}$, accurate to ± 10 percent over the range $300 \leq T_e \leq 3000$ K. At 200K, the third and fourth clusters yield $\alpha(69^\circ) = \alpha(86^\circ) = (3 \pm 1) \times 10^{-6}$ cm³/sec. A new recombination mechanism, cluster-detachment recombination, is postulated to account for the very weak variation of α with electron temperature observed for the (35⁺) and (52⁺) ions.

11. *Photodissociation Spectroscopy of CO₃⁻* – J.T. Moseley, P.C. Cosby, and J.R. Peterson, Stanford Research Institute.

Contract Report No. 321

November 1976

The photodissociation cross section of the carbon trioxide negative ion has been measured over the wavelength range from 457.9 nm to 694.0 nm, and reveals detailed structure reflecting the vibrational spacings of the predissociating excited electronic state. From an analysis of the structure, we identified three vibrational modes of the excited state having energies of 990 cm⁻¹, 1470 cm⁻¹, and 880 cm⁻¹. The bond energy of the carbon trioxide negative ion (to separation into a carbon dioxide molecule and an atomic oxygen negative ion) was determined to be 1.8 ± 0.1 eV, and the electron affinity of carbon trioxide was found to be 2.9 ± 0.3 eV. By comparison with theoretical calculations, the lowest predissociating state was identified as the one doublet A one state. Observations regarding other excited states of the carbon trioxide negative ion are made.

12. *Calculation of Energetics of Selected Atmospheric Systems* – H.H. Michels, United Technologies Research Center.

Report No. AFGL-TR-76-0120

May 1976

Research was directed toward the calculation of the electronic structure and radiative transition probabilities for NO, NO₂, and TiO. Both ab initio methods, employing configuration interaction (CI), and density functional methods (X_α) were utilized.